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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER DAAG29 80 C 0059	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER (12)
4. TITLE (and Subtitle) CHEMICAL DESIGN OF ELASTOMERIC BEHAVIOR		5. TYPE OF REPORT & PERIOD COVERED Final Report 15/Jan./80 to 14/Jan./82
		6. PERFORMING ORG. REPORT NUMBER DRXRO-IP-L-16728-C
7. AUTHOR(s) Jack L. Koenig		8. CONTRACT OR GRANT NUMBER(s) DAAG29 80 C 0059
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Macromolecular Science Case Western Reserve University Cleveland, Ohio 44106		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS U. S. Army Research Office Post Office Box 12211 Research Triangle Park, NC 27709		12. REPORT DATE 4/20/82
		13. NUMBER OF PAGES 16
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) Office of Naval Research The Ohio State University Research Center 1314 Kinnear Road Columbus, OH 43212		15. SECURITY CLASS (of this report) Unclassified
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		15a. DECLASSIFICATION DOWNGRADING SCHEDULE
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) NA		
18. SUPPLEMENTARY NOTES The view, opinions, and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Elastomer - Rubber - NMR - FTIR - Crosslinking - Kinetic - Polybutadiene		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) High resolution magic-angle proton enhanced NMR spectra have been obtained of peroxide crosslinked polybutadiene and sulfur-vulcanized natural rubber. These spectra allow a determination of the crosslink structure in these elastomers. Chemical modification of the structure of the crosslinks have been made.		

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CHEMICAL DESIGN OF ELASTOMERIC BEHAVIOR

- Final Report -

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V. Okocha - M.S. - 1982

20 April 1982

U.S. ARMY RESEARCH OFFICE

Contract No.
DAAG29 80 C 0059

for period
(15 January 1980
to
14 January 1982)

Department of Macromolecular Science
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Accession For	
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CHEMICAL DESIGN OF ELASTOMERIC BEHAVIOR

STATEMENT OF PROBLEM

Although we have utilized elastomers and rubbers in engineering applications for over 140 years, the full potential of elastomeric behavior has not been realized. The problem has been that few relationships exist between the structures of the crosslinks and the mechanical performance of the rubber. The scarcity of knowledge stems not from a lack of study of the system--the voluminous literature bears this out. The difficulties arise from the complex nature of the reactions and the unyielding nature of the polymer with respect to analysis. By definition, the networks are insoluble so traditional chemical and spectroscopic techniques are limited. The number or density of crosslinks is very small requiring sensitive techniques. Thus, the macroscopic behavior cannot be interpreted in chemical or structural terms. Until structure property relationships are established for crosslinked systems, progress in elastomeric materials will be slow. With the knowledge of structure-property relationships for rubbers, special systems can be designed for specific applications.

We proposed to utilize two new instrumental techniques which are particularly suited for studies of elastomeric systems to determine the structure of crosslinks. We proposed using recently developed high resolution nuclear magnetic resonance for the solid state on crosslinked compositions to determine the number and chemical structure of the crosslinks. In addition Fourier transform infrared spectroscopy will be used to monitor and follow the kinetic changes in the structures of the crosslinks. From a study of the chemical or crosslinking reactions, the range of structural crosslinks can be established and related to the physical and mechanical properties. In this manner, a detailed knowledge of the number, kind, and structure of the crosslinks can be obtained.

Coupling these experimental results with recent advances in our theoretical insights should allow the understanding and rational prediction of the macroscopic behavior of networks. In this context, a structural theory should

be of value in designing elastomers and rubbers with special performance attributes for military, aerospace and industrial applications.

SUMMARY REPORT

Using the combined methods of high-power proton decoupling and magic angle sample spinning, it is possible to obtain solid state ^{13}C spectra which have a relatively narrow line width ($\sim 100\text{ Hz}$) and occurring at the isotropic chemical shift positions observed for liquid-state ^{13}C NMR (1,2,3). Hence, using this combination of techniques, one can obtain structural information concerning the nature of the carbons. For our purposes, we are interested in examining crosslinked polymer systems. Our laboratory has a Nicolet ND-150 NMR spectrometer which has been designed with a solid state probe allowing some of the first measurements of solids at high magnetic fields (4). Most of the previous work was carried out at 25 MHz rather than at 150 MHz as with our instrument. However, no previous work had been done in this field with respect to crosslinked rubbers so it was necessary to develop the technique from the beginning. The method has been developed and allows the detection and structural assignment of the different crosslinks and pendent groups as well as the isomerization of the polymer chain which also occurs.

Our initial studies were directed at a model system (cis-polybutadiene) crosslinked with a chemical which would yield simple crosslinks (C-C) in quantitative fashion. Dicumyl peroxide is such a system. The solid state NMR of polybutadiene (uncrosslinked) is shown in Figure 1 while the spectra of cis-polybutadiene crosslinked with 5 phr ROOR are shown with two different pulse delay times in Figure 2. The two different delay times serve to indicate whether substantial differences in the relaxation times of the carbons occur. In this case, no substantial differences are observed. It is clear from the additional resonances near 50 ppm that we are observing effects of the peroxide crosslinking. If one carries out a cross polarization experiment for this same sample, one observes the spectra shown in Figure 3 (compared to the one pulse experiment). The cross polarization experiment is more sensitive to the more rigid portions of the sample

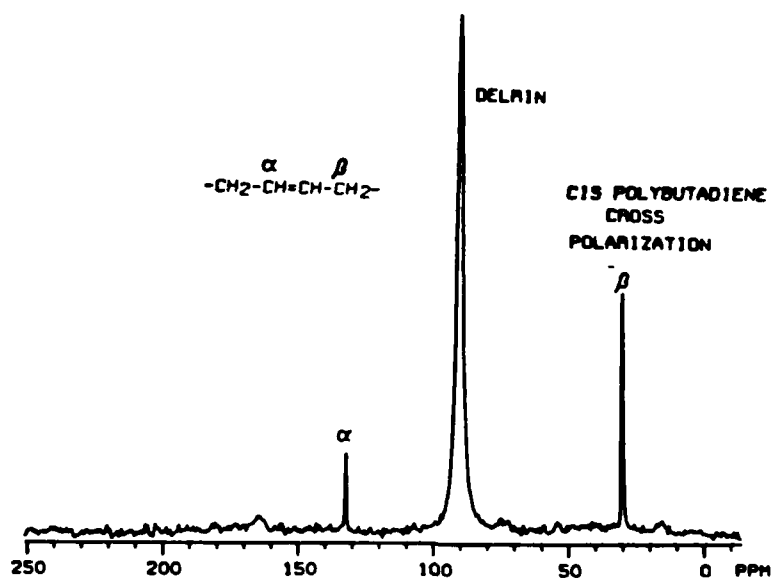


Figure 1.

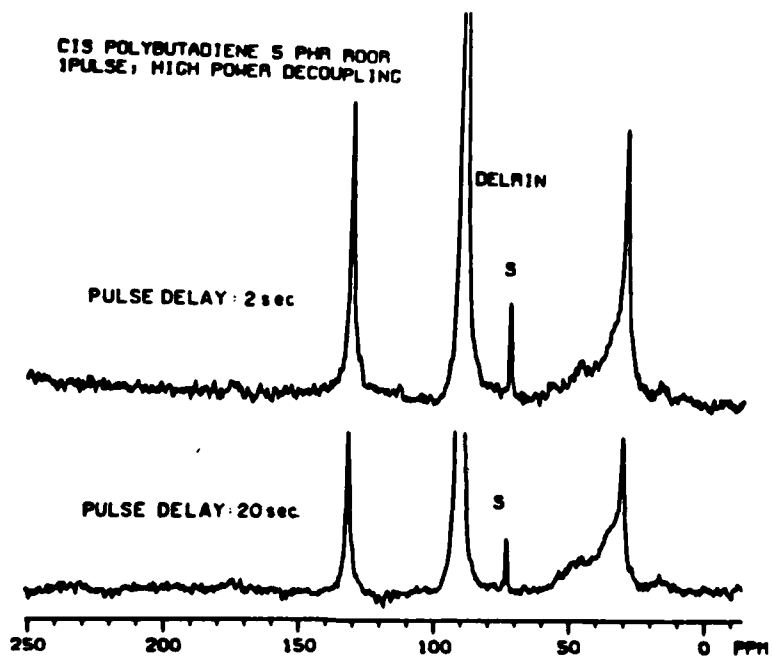


Figure 2.

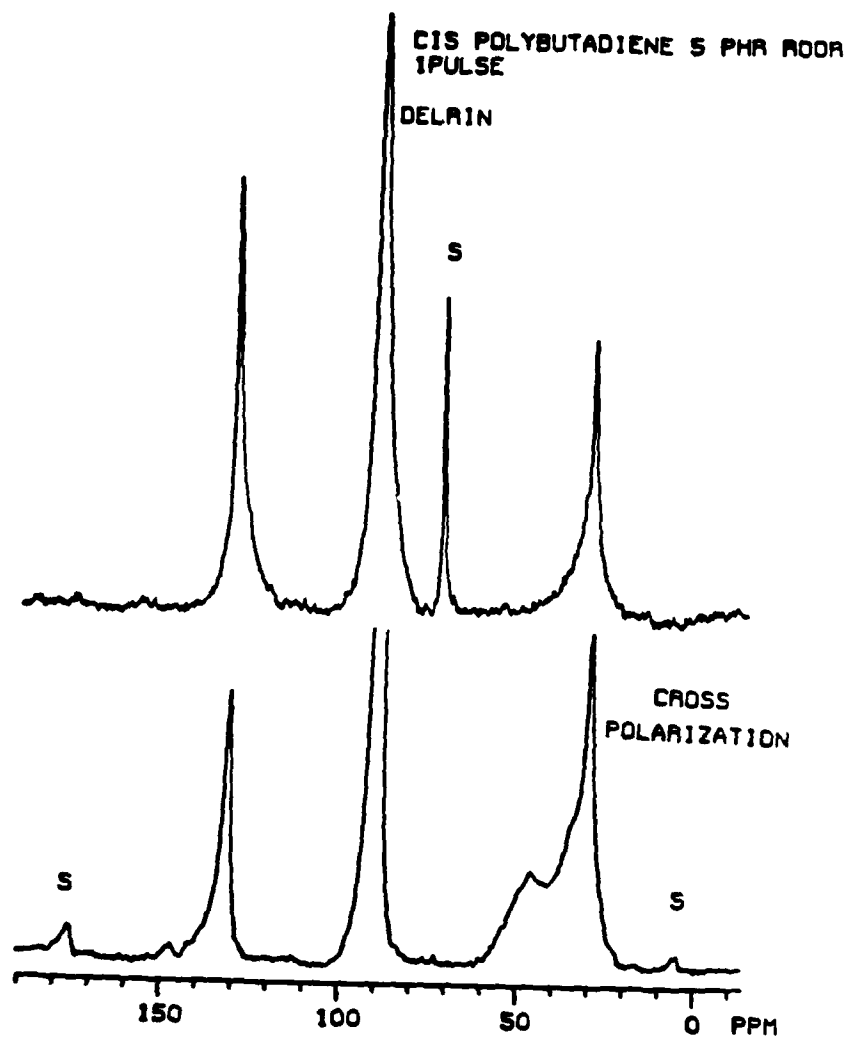


Figure 3.

(i.e. the crosslinks) as is obvious when the two spectra are compared. Additional resonances are also observed on the aromatic carbon near 150 ppm for the cross polarization experiment. We have carried out a number of additional experiments two of which are shown in Figure 4. The highly crosslinked polymer (30 phr ROOR) resin is examined and as expected the new resonances are enhanced as the amount of crosslinking goes up. We have also carried out a pulse sequence which suppresses the resonances of all non-quaternary carbons (i.e. carbons bonded to hydrogen) and a major portion of the resonances arising from crosslinking is suppressed. This experiment is imperfect in that the resonances of the noncrosslinked portion of the polymer cannot be suppressed at the same time as the crosslinked portion due to the higher mobility of the uncrosslinked butadiene resin. However, near 50 ppm we have clear evidence of quaternary carbon resonances indicating the formation of these structures. No other analytical method exists for detecting these structures.

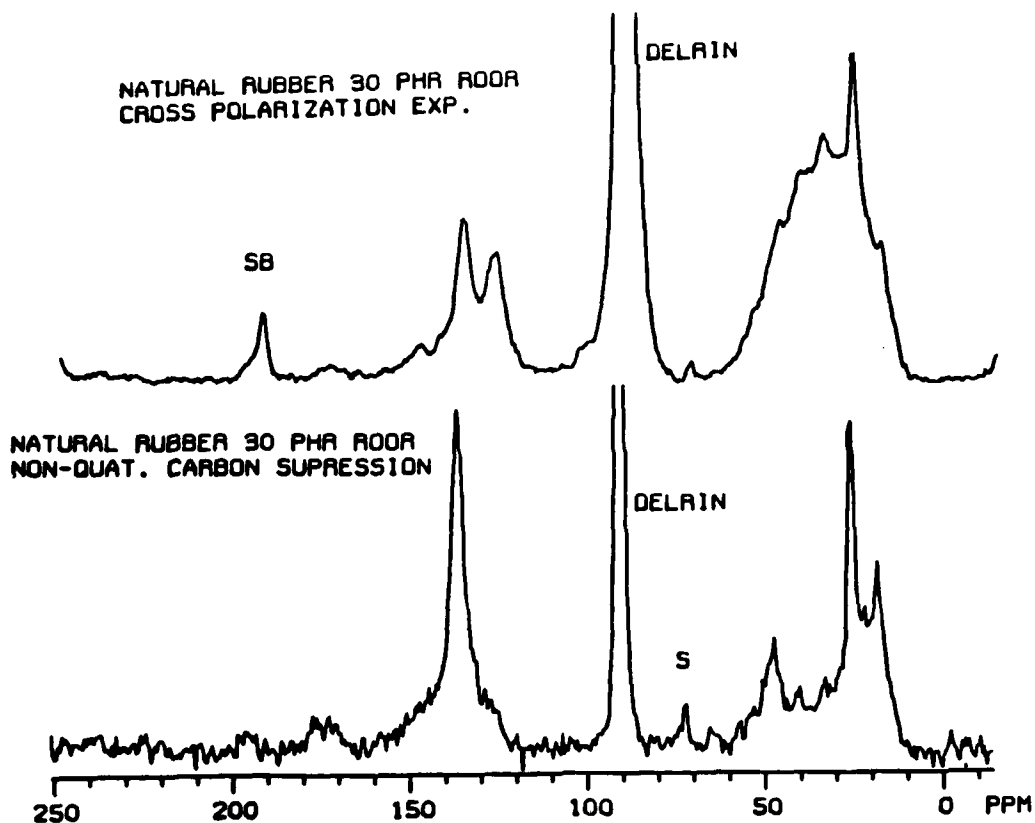
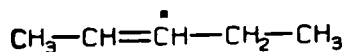


Figure 4.

Since these resonances arising from the crosslinking have not been observed before, their assignment to the various structures needs to be made. The structural assignment can be made using Grant-Paul additivity relationships as shown in Figure 5. The procedure for carrying out the calculation is also shown. We have made the calculations of the expected resonances for a number of different crosslink structures. Figures 6 and 7 demonstrate the results (in stick spectral form) for two different possible crosslinked structures. The new resonances are clearly in the vicinity observed experimentally and offer the possibility of assigning the observed resonances to the structures in the crosslinked network. This

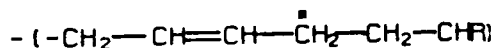
CALCULATION OF CARBON -13 CHEMICAL SHIFTS

OLEFIN CARBONS



$$\begin{aligned} {}^{13}\overset{\blacksquare}{\text{C}} &= (123.31 + 1\cdot\alpha + 1\cdot\beta + 1\cdot\alpha') \\ &= 123.3 + 10.6 + 7.2 + -7.2 \\ &= 133.2 \text{ PPM} \end{aligned}$$

ALIPHATIC CARBONS

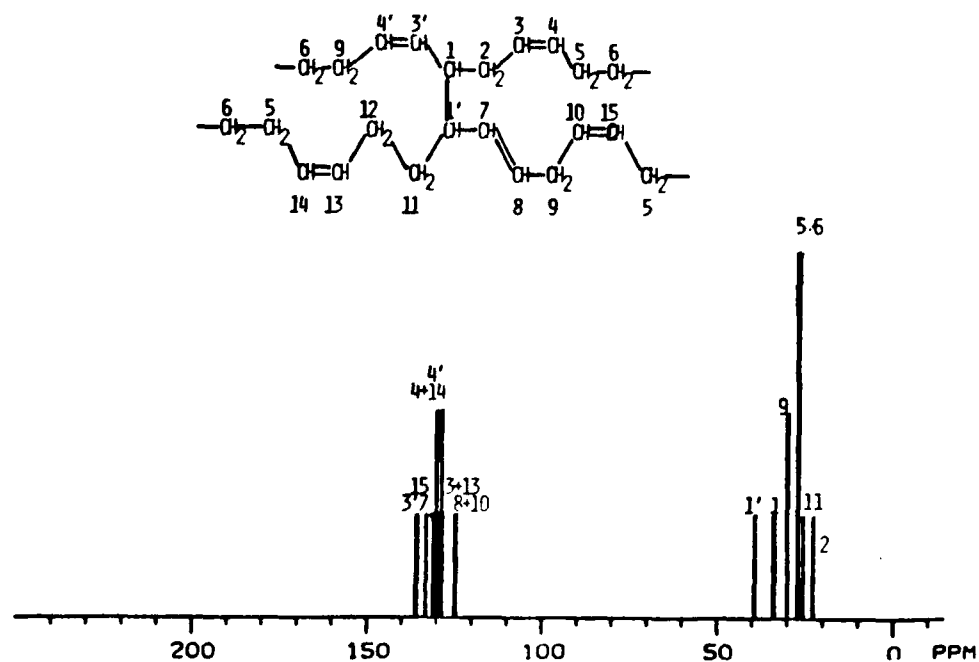


$$\begin{aligned} {}^{13}\text{C} &= 29.9 + \text{CIS C=C} + \text{CH}_2 + \text{CH} \\ &= 29.9 - 2.5 + 0 - 2.5 \\ &= 24.9 \text{ PPM} \end{aligned}$$

Figure 5.

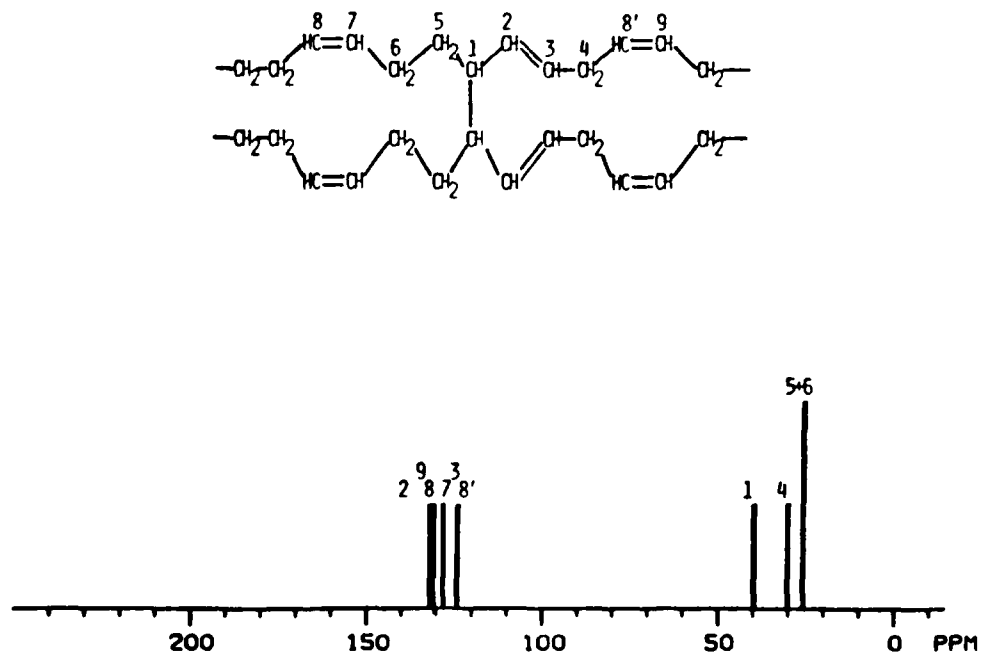
COMBINATION OF A CIS AND AN ISOMERIZED POLYBUTADIENE RADICAL CHAINS

Figure 6.



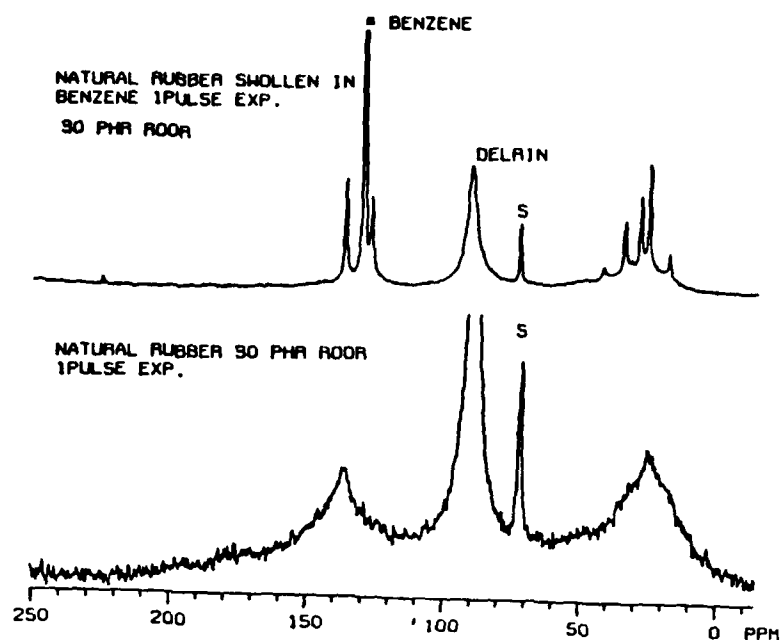
COMBINATION OF TWO ISOMERIZED (CIS - TRANS) POLYBUTADIENE CHAINS

Figure 7.



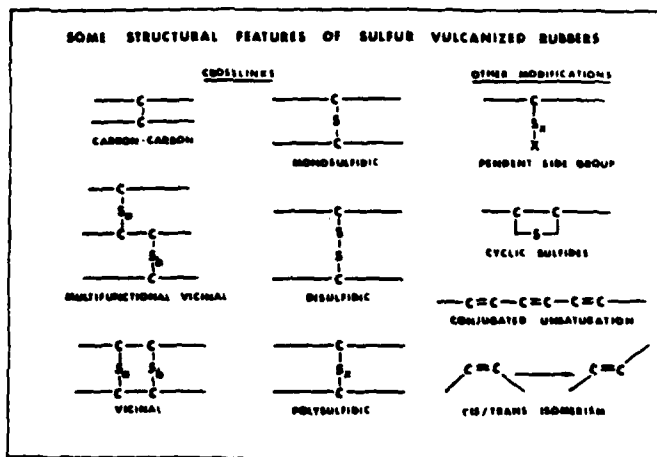
project is continuing. We have found that swelling the crosslinked rubber with benzene gives the network more mobility and sharper resonances are observed. This result is shown in Figure 8 for peroxide crosslinking of natural rubber. The improved resolution occurs with swelling of the rubber with benzene.

Figure 8.



In addition to this project, we have also been studying sulfur vulcanization of natural rubber. In Figure 9, a diagram is given of the different structural features expected in sulfur vulcanized rubbers. Figure 10 gives the NMR in the solid state of the cis and trans isomers of 1,4-polyisoprene.

Figure 9.



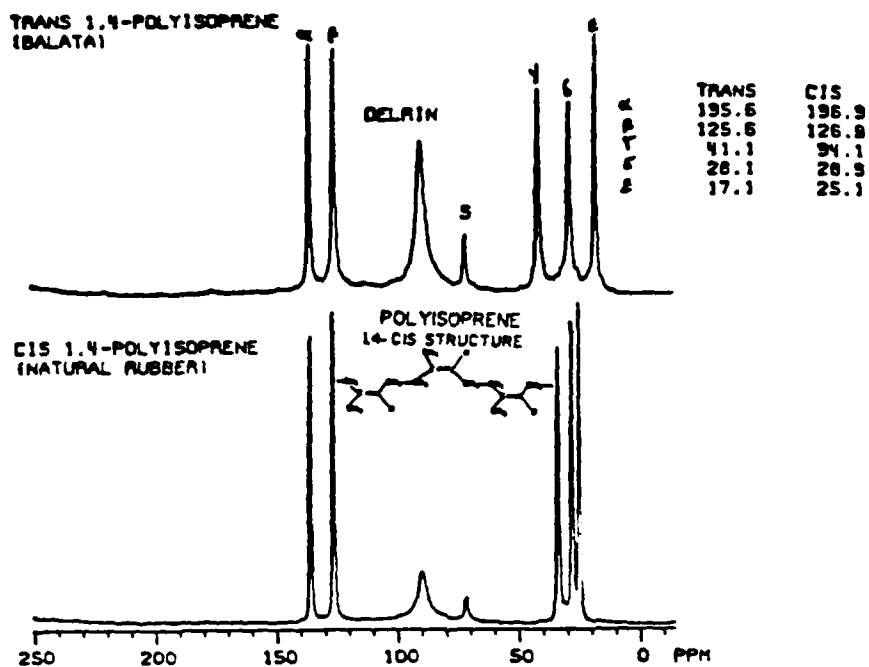


Figure 10.

In Figure 11, we show two spectra of natural rubber which have been cured with 20 phr TMDD/2PHR sulfur at 160°C for 30 minutes and a spectra of natural rubber cured with only 10 phr of TMDD at 160°C. The spectra are quite different and show that a very different network structure has been formed. Some of the resonances have been assigned based on additivity calculations of the type previously mentioned. Observe particularly that we can for the first time differentiate between the mono, di, and polysulfidic links. Hence, we have an analytical method which can be used to follow the changes in the network structure with the amount of sulfur and accelerator, and variations in time and temperature. Such measurements were not possible in the past.

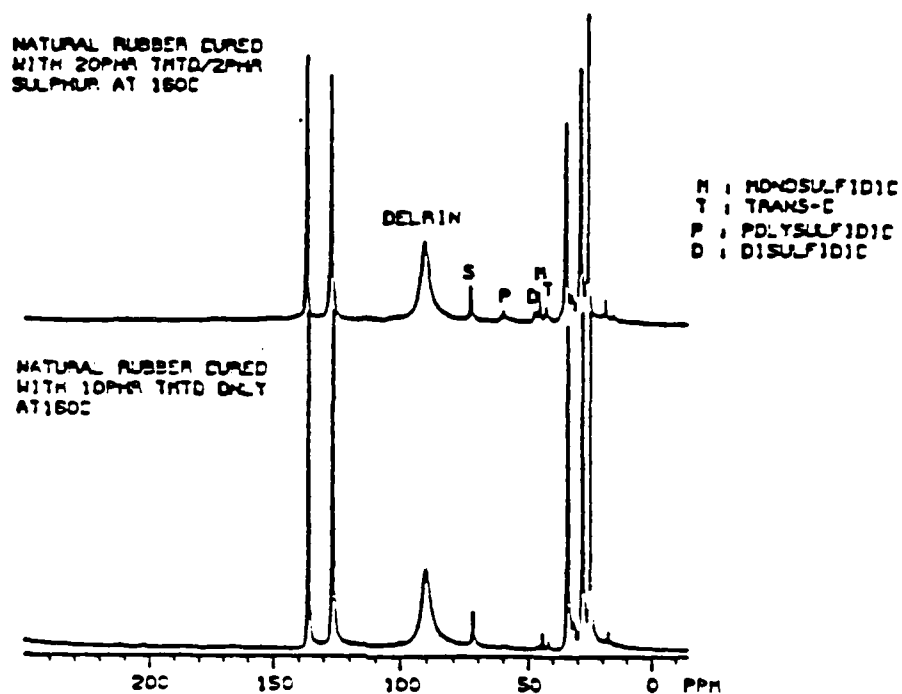


Figure 11.

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- V. Okocha, and J.L. Koenig, "Solid State NMR Measurements of Sulfur-Vulcanized Natural Rubber", in progress.

SUPPORT OF PERSONNEL

Professor J.L. Koenig		Partial Support
C.H. Chen	Ph.D. 1981	Partial Support
V. Okocha	M.S. 1982	Partial Support
D. Patterson	M.S. 1982	Full Support